

# Utilisation of isotopic oxygen exchange in the development of air-purification catalysts

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## 1 Introduction

Isotopic oxygen exchange experiments give information on oxygen mobility on the catalytic surface. Examples of the reactions where this surface mobility is important are for instance steam reforming, water gas shift, hydrocarbon oxidation, aromatic hydrogenation, methanol synthesis, coke formation, oxygen storage in three-way catalysts, certain selective oxidation reactions, reactions involving a 'spillover' of reactive species etc.

There are three types of exchange of dioxygen on oxide catalysts, namely, the homoexchange or isotopic equilibration, the simple heteroexchange and the multiple heteroexchange (Boreskov, 1964). Equilibration experiments (homoexchange) give information about the nature and surface area of metal particles, and the experiments are normally carried out with equimolar mixtures of certain gas molecule and its isotopic counterpart. Heteroexchange, or simply, isotopic exchange experiments, can be used to reveal e.g. diffusion coefficients on the surface of catalysts. The isotopic exchange experiments can be carried out with pure isotopic gas. (Duprez, 2006)

Isotopically labelled molecules can also be used in reaction mechanistic studies. For example, it can be concluded from isotopic experiments, which of the existing oxygens (i.e. oxygen from the gas-phase or oxygen from catalytic surface) takes part in the catalytic oxidation reactions.

## 2 Objectives of the research

The objectives of this study are (1) to prepare novel sample catalysts, (2) to study catalysts activity in oxidation of organic compounds, (3) to reveal the surface oxidation mechanisms and oxygen mobility related to the catalysts, (4) to obtain information on the catalyst deactivation, and (5) to improve the catalyst composition to achieve high performance of the catalyst in oxidation applications.

## 3 Results

At the beginning, Pd/Al<sub>2</sub>O<sub>3</sub> catalysts have been studied. The catalysts have been prepared by incipient wetness impregnation with Pd-nitrite complex formation from NaNO<sub>2</sub> and Pd(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O aqueous solutions following the preparation explained by Benkhaled et al. (2006). The further preparation of the catalyst samples was then slightly different. One part of the catalysts was washed after calcination (Pd-w) and the second part of the catalysts was reduced before washing (Pd-rw). The third part of the catalysts was not washed after calcination at 200°C, and it is called as Pd-dry. More detailed information on catalyst preparation can be found from Ref. Ojala et al. (2010).

The catalysts were characterized by several different methods including XRD, BET, BJH, H<sub>2</sub> chemisorption, ICP, FTIR and CH<sub>4</sub> as well as H<sub>2</sub>-TPR. In addition, isotopic oxygen exchange and equilibration with oxygen

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( $^{18}\text{O}_2$ ) and carbon dioxide ( $\text{C}^{18}\text{O}_2$ ) were carried out. The activities of the catalysts in methane oxidation were compared and the reaction mechanism was studied with the aid of labelled oxygen.

### 3.1 Catalyst characterization

The results of catalyst characterization are presented in Table I.

**Table I** Characterization of the catalysts.

	Residual Na (w-%)	Amount of Pd (w-%)	BET ( $\text{m}^2/\text{g}$ )	Dispersion (%)
Pd-dry	1.097	0.86	183	35.5
Pd-w	0.378	0.86	188	26.1
Pd-rw	0.615	0.87	230	16.3

Characterization shows that, in general, washing reduces the amount of residual Na, but does not affect the amount of Pd. BET surface area is increased for further treated catalysts but, at the same time, the dispersion is decreased. According to BJH, the pore size of the Pd-rw catalyst is slightly smaller and total pore volume is higher than those for other two catalysts. XRD measurements showed also that the crystal size of alumina in the Pd-rw catalyst is slightly smaller.

### 3.2 Isotopic experiments

The isotopic experiments were carried out in a closed recycle reactor, which was coupled with a mass spectrometer. The recycle pump was used to avoid any diffusion effect in the gas phase, which may affect the partial pressures measured by the mass spectrometer. Prior to the isotopic experiments, the catalysts were either pre-oxidized in  $\text{O}_2$  flow or pre-reduced in  $\text{H}_2$  flow for 15 min.

Isotopic oxygen exchange with  $^{18}\text{O}_2$  and equilibration with  $^{18}\text{O}_2+^{16}\text{O}_2$  were carried out with all the catalysts. Similarly experiments with  $\text{C}^{18}\text{O}_2$  and  $\text{C}^{16}\text{O}_2 + ^{18}\text{O}_2$  were done. It was seen that, in general, in oxygen exchange the pre-reduction of the catalyst enhances the activity. The oxygen exchange or equilibration did not occur at lower test temperatures (200 and 300°C), but it appeared at 400°C. Oxygen activation over the alumina support was not significant even at 500°C.

In the case of  $\text{C}^{18}\text{O}_2$  exchange, the rates of exchange are increased due to carbonate formation on the catalyst, the presence of which was verified with in situ FTIR-measurements. In addition,  $\text{C}^{18}\text{O}_2$  exchange takes place at remarkably lower temperatures than  $^{18}\text{O}_2$  exchange. It was observed that  $\text{CO}_2$  exchange occurs mainly on  $\text{Al}_2\text{O}_3$  whereas the exchange of  $\text{O}_2$  occurs preferably on completely or partially reduced palladium. It was also observed during the  $^{18}\text{O}_2+\text{C}^{16}\text{O}_2$  equilibration experiment that  $\text{C}^{18}\text{O}^{16}\text{O}$  was formed already at temperature of 350°C.

In general, the Pd-alumina catalysts are not very active in isotopic oxygen exchange compared with other noble metals. However, the oxygen activation was improved with pre-reduction, further treatment of the catalyst and the presence of  $\text{CO}_2$  in the reaction mixture. Thus, of the tested catalysts, the most active sample was Pd-rw.

### 3.3 Methane oxidation

Methane oxidation experiments were carried out in continuous tubular reactor with a mixture of nitrogen (89.5 vol-%), oxygen (19 vol-%) and methane (5 vol-%). The experimental procedure consisted of series of light-off tests done periodically by heating and cooling the reactor. Between heating and cooling the stability of the catalyst was followed at constant temperature. Table 2 shows the results of methane oxidation experiments.

**Table 2** Results of methane oxidation.

	Light-off temperature ( $T_{50}$ ) (°C)	Conversion at 400°C for 1 <sup>st</sup> experimental run (%)	Conversion at 400°C for 2 <sup>nd</sup> experimental run (%)
Pd-dry	not reached, evaluated ~430	40	25
Pd-w	400	45	33
Pd-rw	380	55	55

The oxidation results showed that the Pd-rw catalyst was the most active and it also kept its stability during the experimental run.

The experiment carried out with methane and labelled oxygen over pre-reduced catalysts showed that the first reaction product appearing in the gas-phase was  $C^{16}O_2$ . It means that methane reacts first with oxygen available on the catalytic surface. The necessity of surface oxygen was also seen in the experiment that was carried out with 'decomposed PdO' (pre-treatment at 700°C in vacuum) over which the  $CH_4$  oxidation started only after a slight delay at the beginning. In that experiment  $CH_4$  was fed with  $^{18}O_2$  and rapid formation of  $^{16}O^{18}O$  was seen before the oxidation started. The enhancement in the oxygen exchange in the presence of methane can also be due to the formation of  $CO_2$  as a reaction product. It was seen previously that carbonates formed from gaseous  $CO_2$  enhance the rate of oxygen exchange (Ojala et al. 2010).

It has been previously suggested by Castellazzi et al. (2009) that the methane oxidation over Pd-based catalysts starts at the temperature where methane is able to reduce PdO. We also marked, that the catalyst Pd-rw, that was the most active and stabile catalyst in methane oxidation was the one that was easiest to reduce. However, we were not able to match exactly the starting temperature of  $CO_2$  formation in methane oxidation and the starting temperature of  $CH_4$ -TPR. The Pd-rw catalyst has the largest Pd particle size that has reported to facilitate the reduction compared to Pd having smaller particle sizes. This may explain the improved activity of the Pd-rw sample compared with other two catalyst samples.

## 4 Relevance of the research

The research described promotes the understanding of the catalytic reaction mechanisms and thus contributes to the design of better catalysts and catalytic reactors for emission treatment. This kind of fundamental research is necessary in the development of catalytic processes whose objective is the improvement of the state of our environment.

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